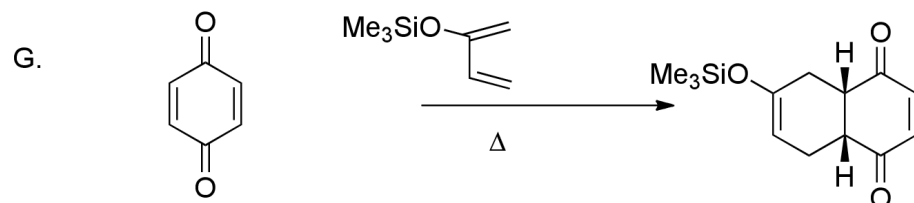
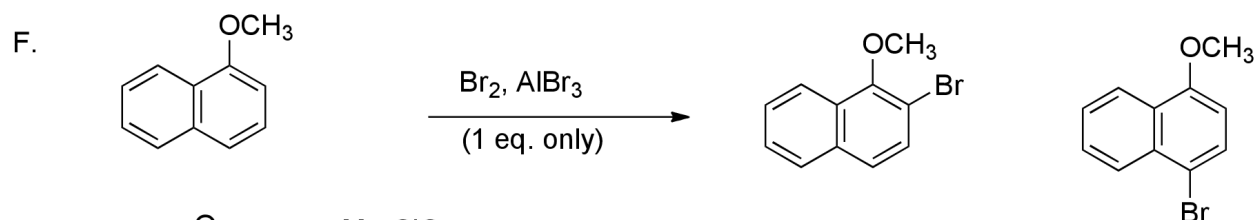
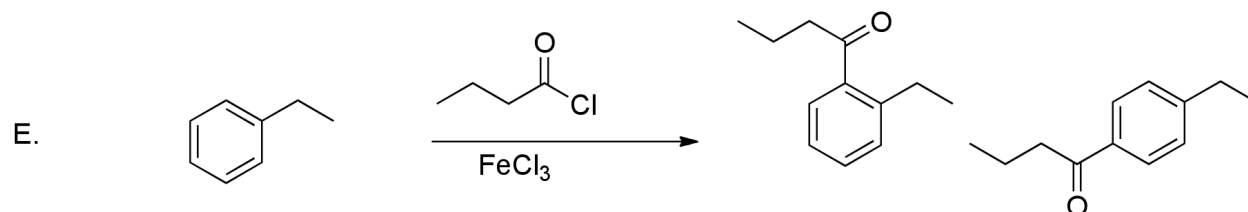
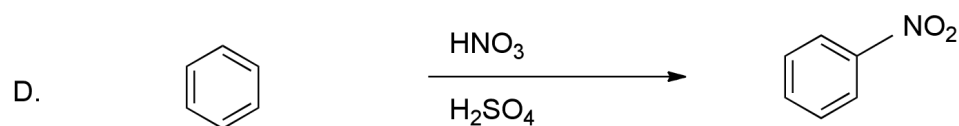
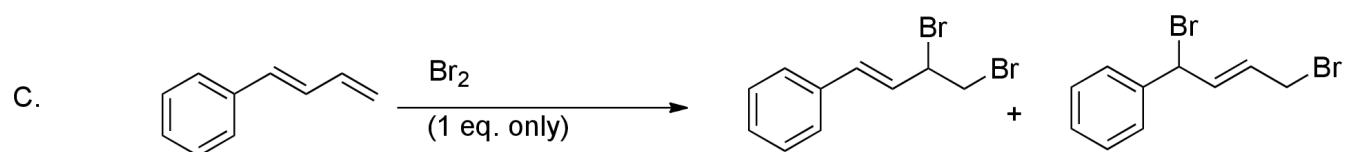
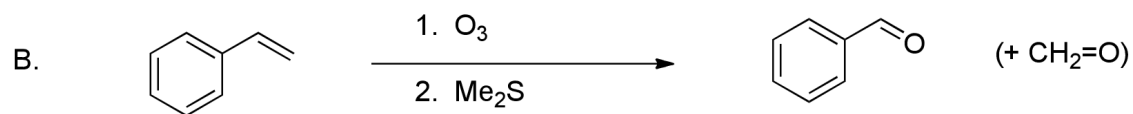
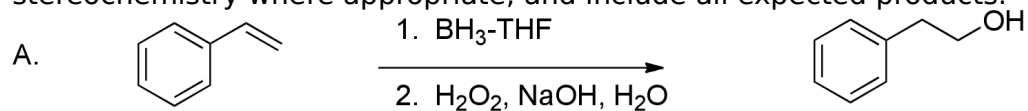
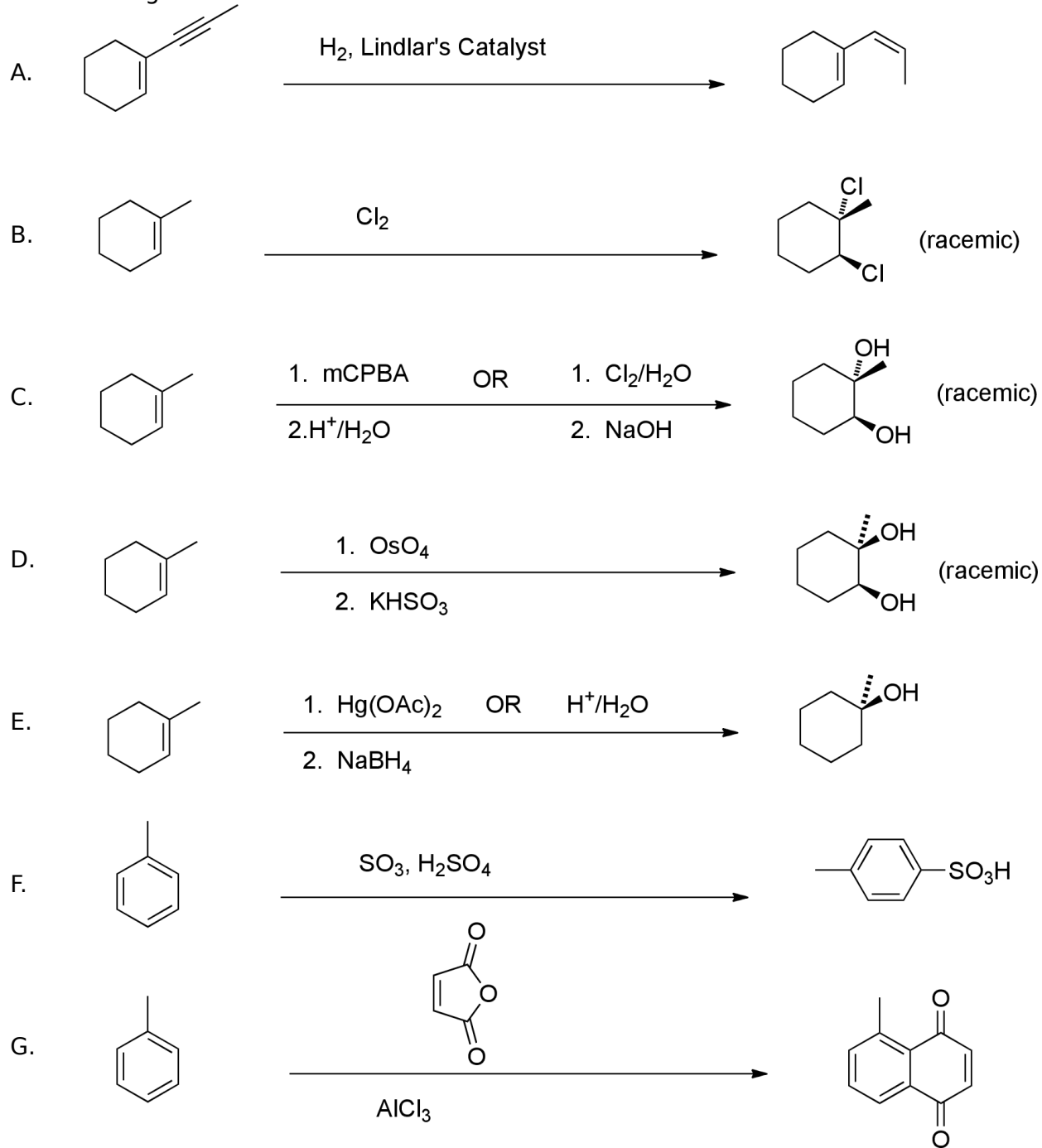




1. (35 points) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected products.

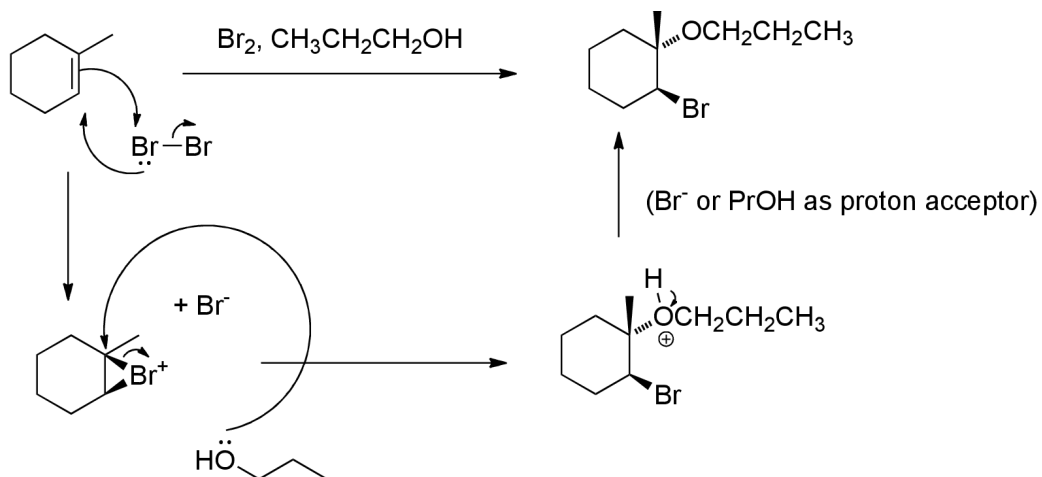


2. (35 points) Write (over the arrow) the reagents and/or conditions needed to accomplish the following transformations.

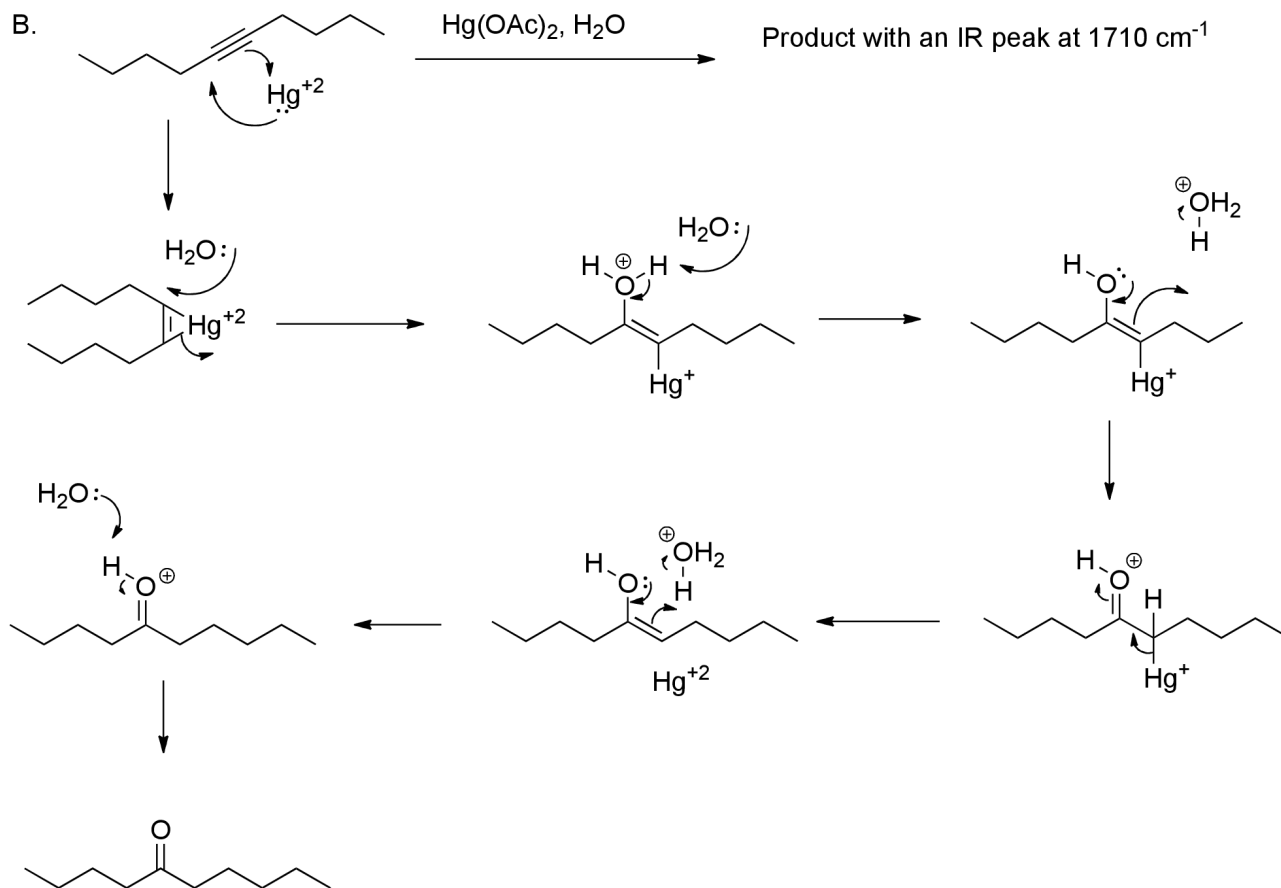


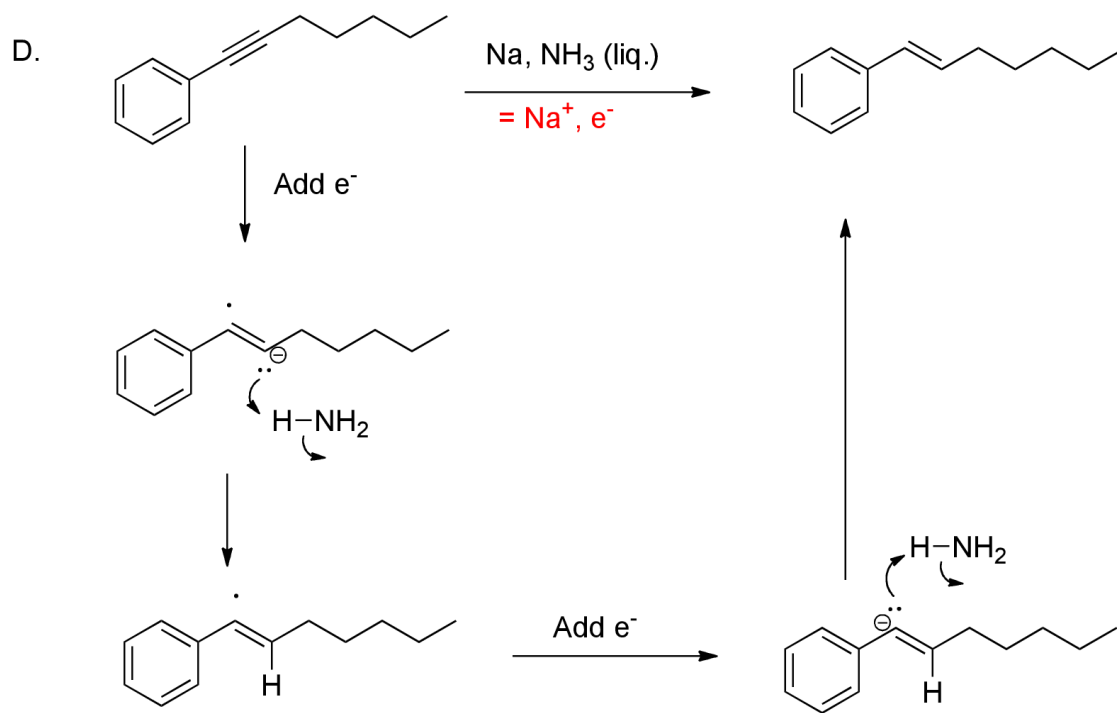
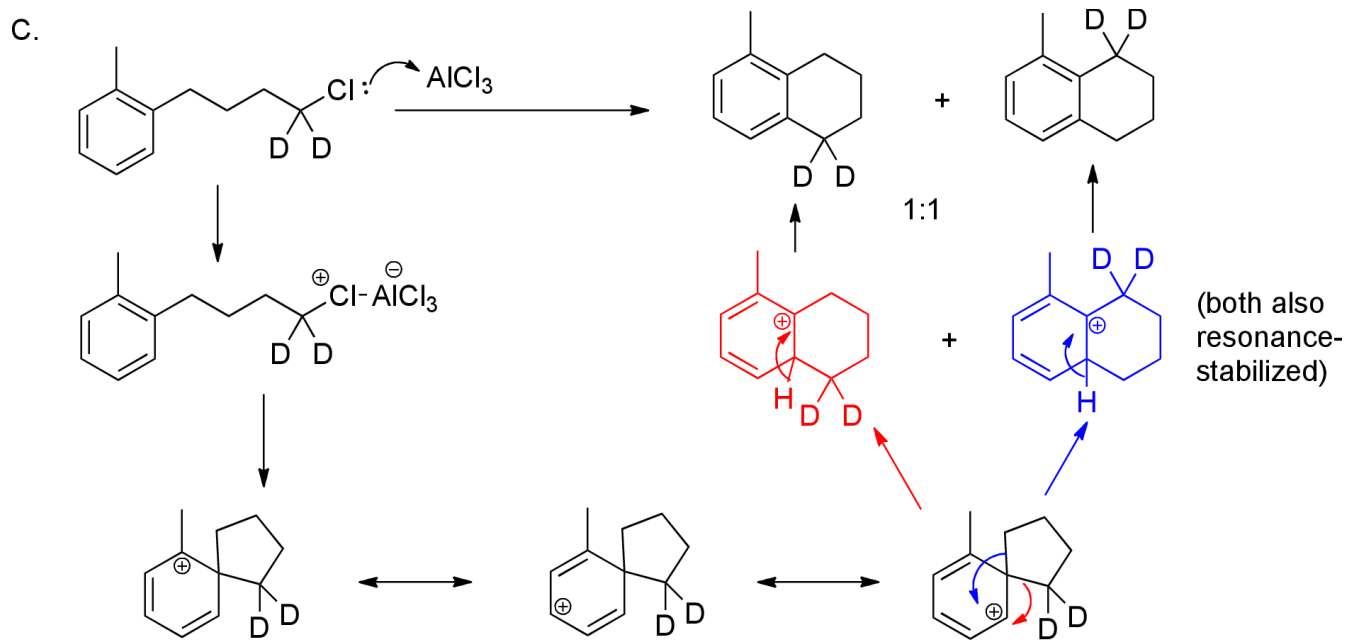
3. (28 points) Write multistep mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations. Be sure to draw resonance structures for any intermediate so stabilized.

A.



B.



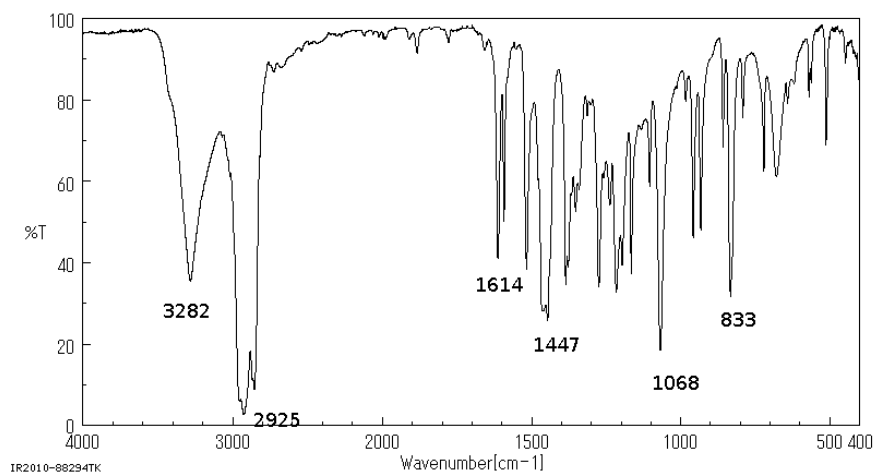


4. (25 points) A molecule has the molecular formula  $C_8H_{10}O_2$ .

A. How many degrees of unsaturation does it have?

$$(2 \times 8 (\#C) + 2 - 10 (\#H)) / 2 = 4$$

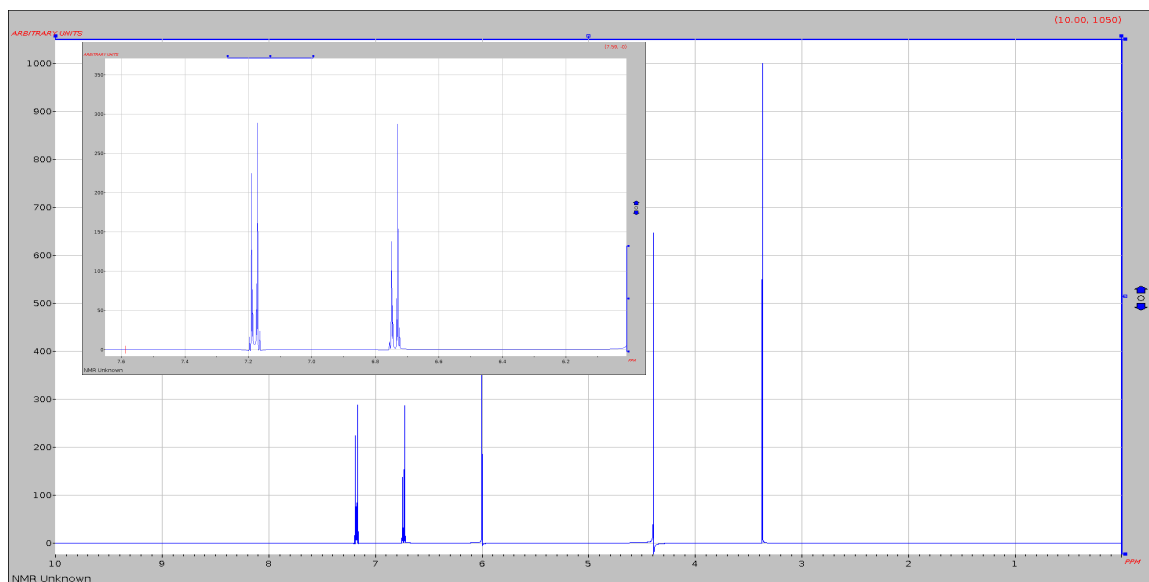
B. The infrared spectrum is shown below. Circle any peaks that tell you what functional groups are present, and list those functional groups. Several peaks are identified to help you estimate the scale.



3282: O-H (sharper than normal, but the other alternative—N-H—is not possible because of the molecular formula.)

2925: C-H.

C. The  $^1\text{H}$  NMR with expansion (6-7.5 ppm) is shown below; integrations are listed below the spectrum. Propose a structure that is consistent with all this data. (Failing a complete structure, suggest what fragments are present for partial credit.)



Integrals:

7.18 ppm: 2H

6.74 ppm: 2H

6.00 ppm: 1H

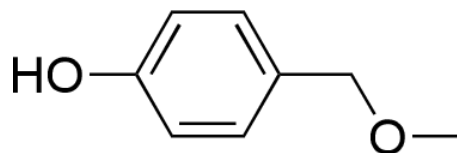
4.39 ppm: 2H

3.37 ppm: 3H

4 DoU suggests an aromatic compound, confirmed by the two doublets in the aromatic region (6.74/7.18). Because we see two doublets (2H each) this must be a para-disubstituted benzene.

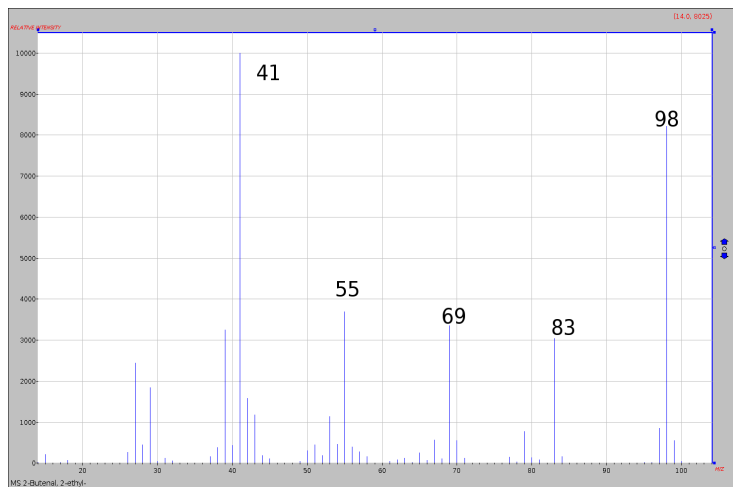
Since we know we have an OH from the IR, we can assign this to the 1H signal at 6.00 ppm.

The other two signals, a  $\text{CH}_3$  and a  $\text{CH}_2$  group, are both fairly far downfield—the  $\text{CH}_2$  more so than the  $\text{CH}_3$ . We have a second oxygen to explain, as well. If both are bonded to the second oxygen, everything fits. The two benzene substituents are  $-\text{OH}$  and  $-\text{CH}_2\text{OCH}_3$ .



5. (25 points) The mass, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra for a compound are shown below.

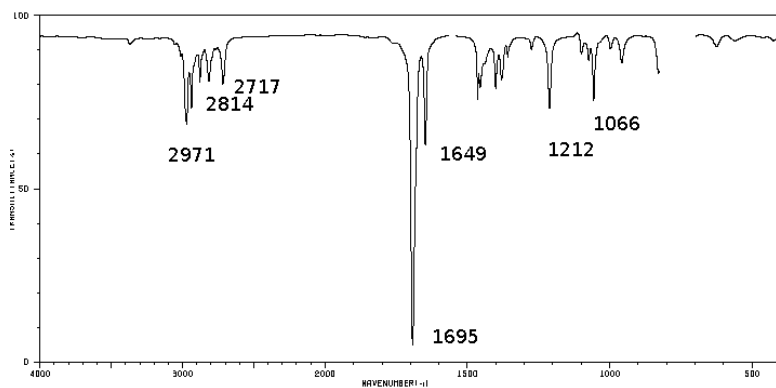
MS:



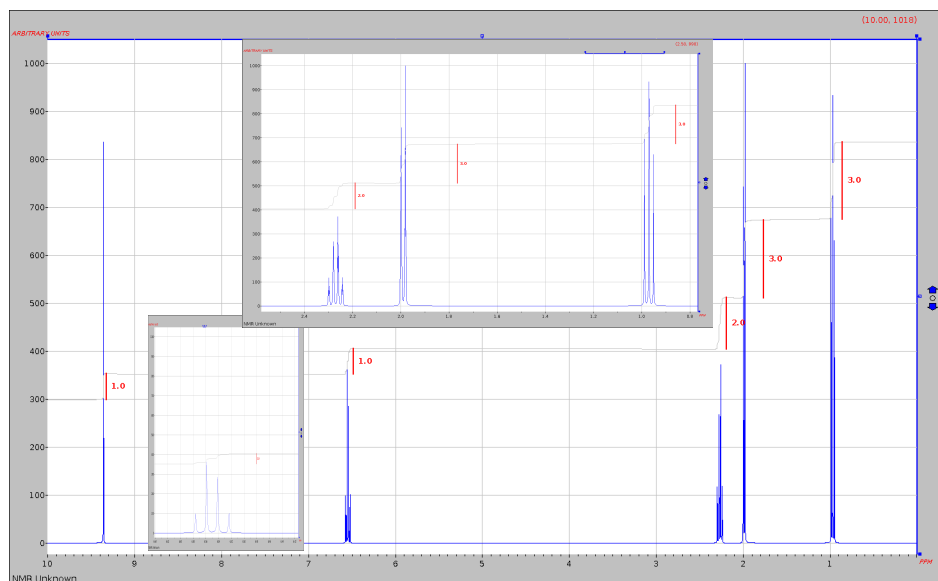
Partial peak listing:

Mass	Intensity, % of base
41.0	100.0
42.0	15.9
43.0	11.8
44.0	1.9
55.0	36.9
56.0	4.0
69.0	33.6
70.0	5.5
71.0	1.2
83.0	30.4
84.0	1.7
97.0	8.6
98.0	82.2
99.0	5.6

IR:



<sup>1</sup>H NMR (insets are 0.5-2.5 ppm above; 6.2-6.8 ppm below):



Integrals:

- 9.36 ppm 1H
- 6.55 ppm 1H
- 2.27 ppm 2H
- 1.99 ppm 3H
- 0.97 ppm 3H

<sup>13</sup>C NMR:

- 194.84
- 149.42
- 146.38
- 16.96
- 14.51
- 12.99

(continued next page)



A. From the mass spectrum (and clues in other spectra), deduce the molecular formula.

The parent ion at 98 has an (M+1) peak that is 6.6% as intense—so 6 carbons (72 mass units). There is a C=O evident in the IR, so there must be oxygen (16 more mass units—total 88). By difference, there are 10 hydrogens, and this matches the total integration in the  $^1\text{H}$  NMR.

### **$\text{C}_6\text{H}_{10}\text{O}$**

B. Propose a structure that fits the data. (If you cannot come up with a complete structure, provide as much analysis of the data as you can.) Be sure to:

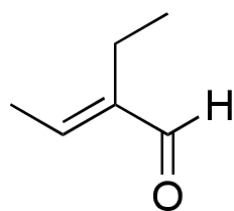
- Calculate the degrees of unsaturation
- Specify functional groups, the evidence you use to identify them, and the impact on the DoU count
- Identify coupling relationships that allow you to identify structural pieces
- Any corroborating evidence you can see that confirms the structure.

2 degrees of unsaturation; one of these is the C=O seen in the IR.

Looking at the  $^{13}\text{C}$  NMR, we also see (in addition to the C=O at 194.84 ppm) two carbons in the  $\text{sp}^2$  region (149.42, 146.38), so there is a C=C double bond and no ring.

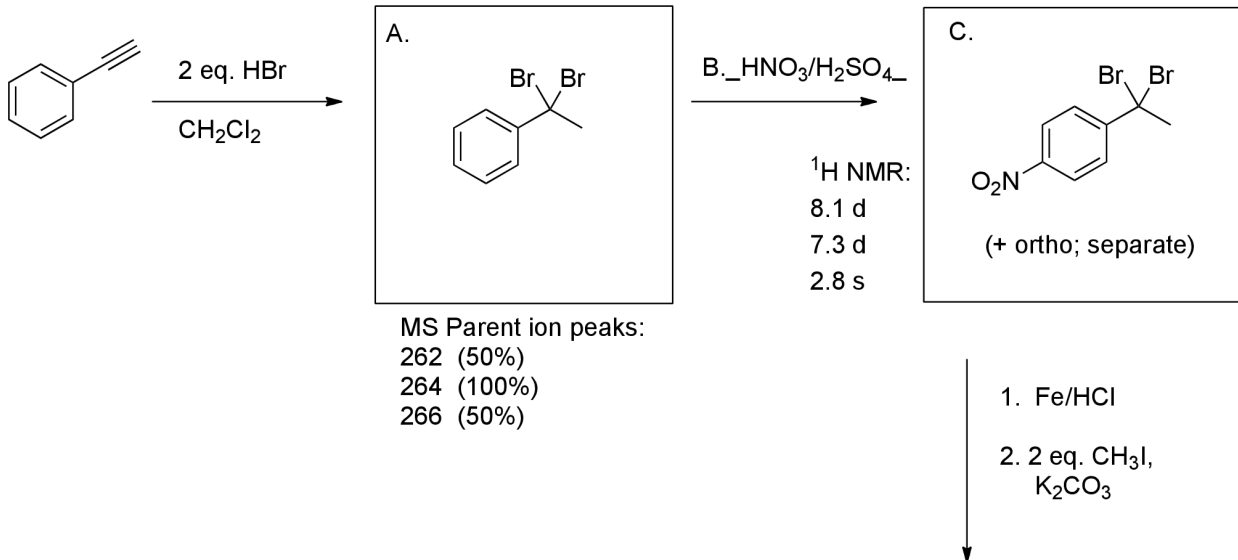
The  $^1\text{H}$  NMR shows us one vinyl C-H proton (6.55 ppm) only, so the double bond is trisubstituted. This is a quartet, so there is a  $\text{CH}_3$  group on the double bond, confirmed by a quartet at 1.99 ppm (in the right chemical shift area, too).

The remaining  $^1\text{H}$  NMR signals are at 9.36: a 1-H singlet; this tells us we have an aldehyde as one substituent on the double bond (uncoupled to any other hydrogens). The remaining signals—a 2-H quartet and a 3-H triplet—are signatures for an ethyl group.

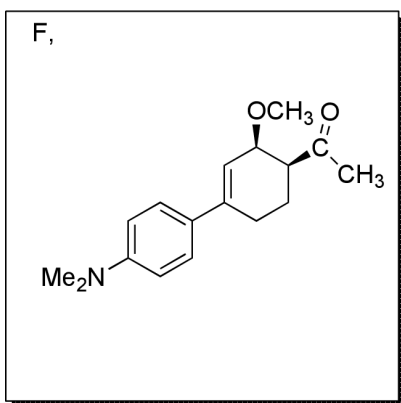
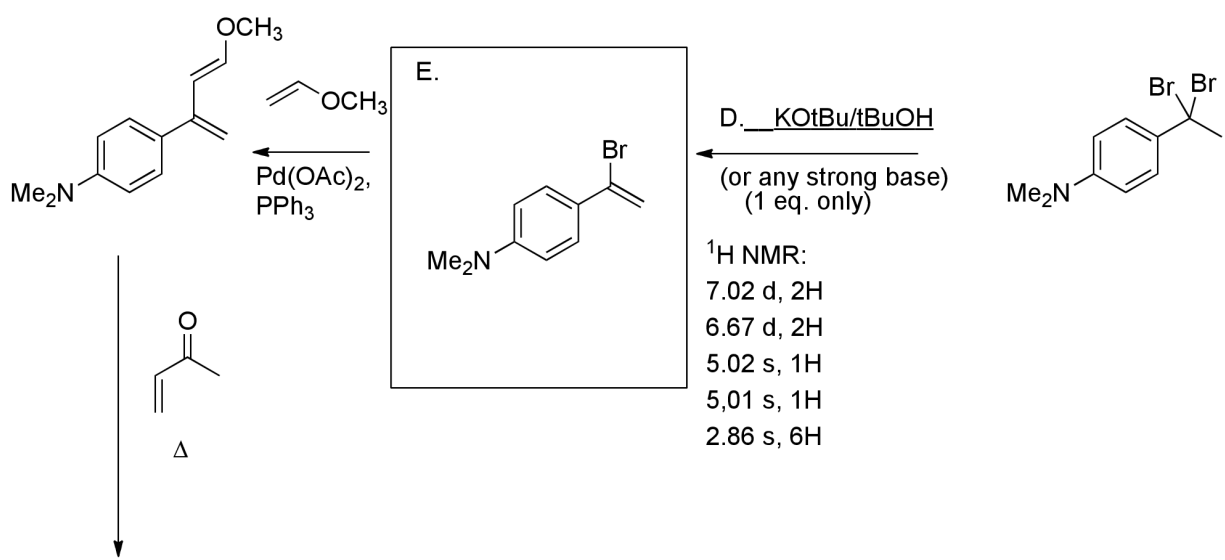


Could be E or Z--no way to distinguish with our data)

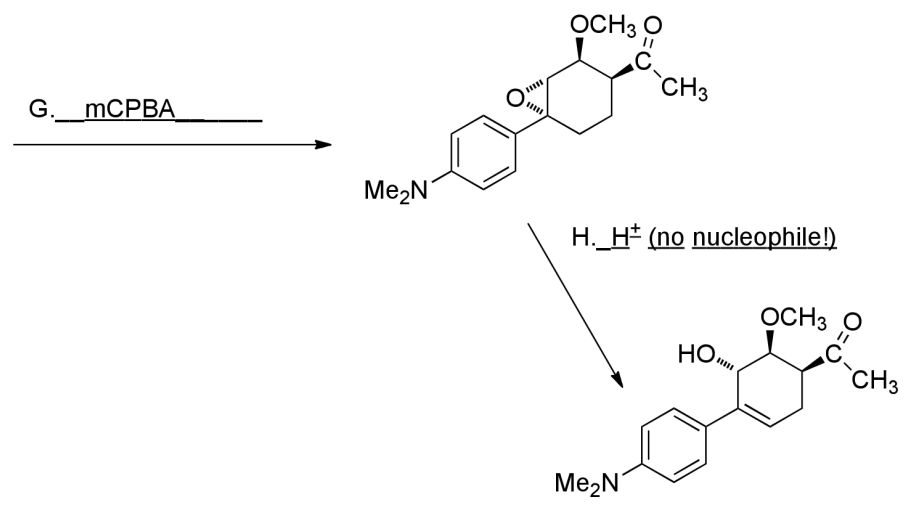
6. (32 points) Fill in the missing intermediates or reagents in the following multistep synthesis.



MS Parent ion peaks:  
 262 (50%)  
 264 (100%)  
 266 (50%)

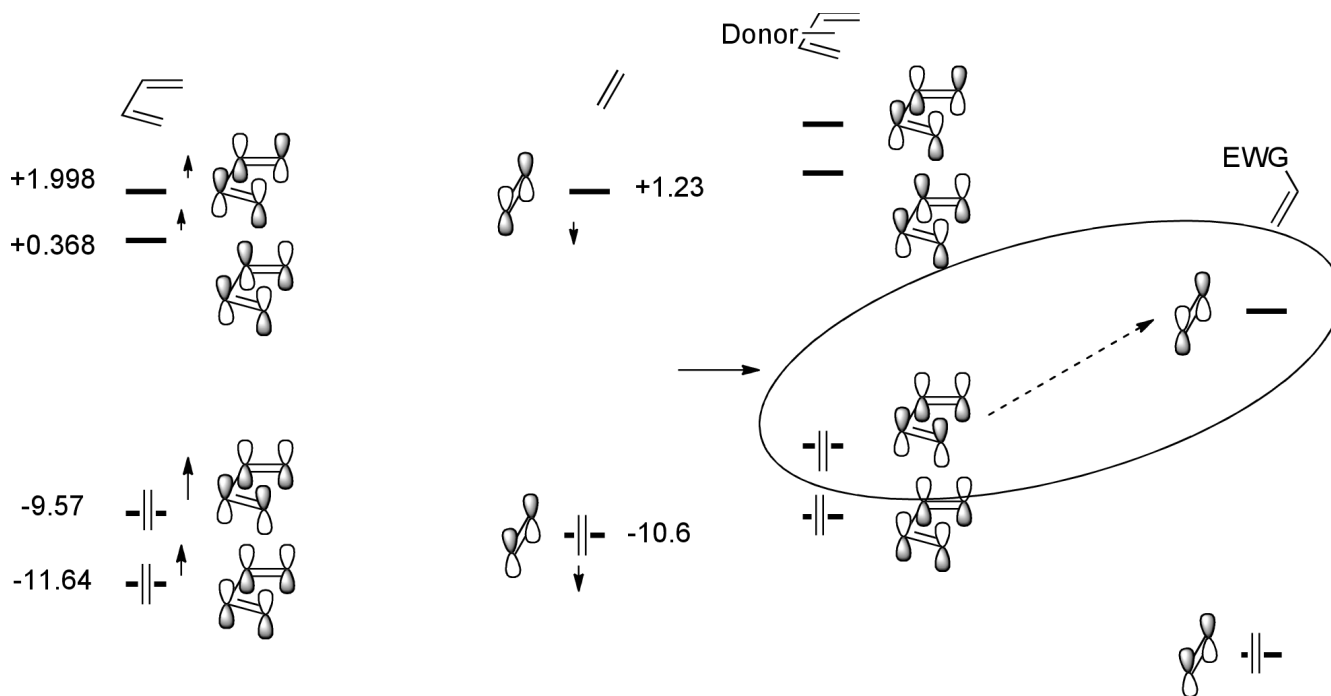


IR:  $1725\text{ cm}^{-1}$



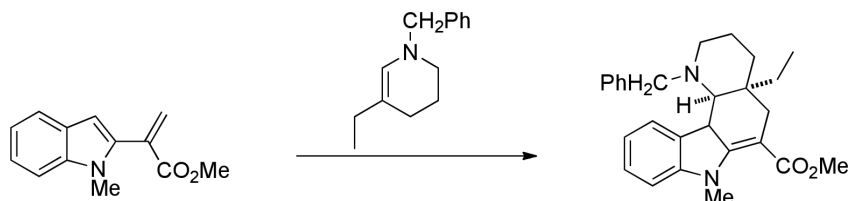
7. (20 points) Normally, the Diels-Alder reaction involves a diene with an electron-donating group reacting with a dienophile that has an electron-withdrawing substituent.

A. Based on the MO diagram below depicting the orbitals in the unsubstituted case (and their energies, in eV), describe why this particular pair of substituents enhances the Diels-Alder reaction. Use the molecular orbital description of the bonding in the reactants and the transition state.

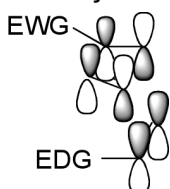


An electron donating group will shift the energies of the diene MOs UP because of destabilization due to electron-electron repulsion. An electron-withdrawing group will move the MOs of the dienophile DOWN, moving the LUMO closer to the energy of the diene HOMO.

B. There are examples of what are called “inverse demand” Diels-Alder reactions, where the electron donor is on the dienophile, and the electron-withdrawing group is on the diene. An example is shown:



In the diagram below, shade in the phases of the orbitals to represent the major HOMO-LUMO interaction in the transition state for this inverse-demand Diels-Alder reaction. (Hint: think about how you would adapt your answer to Part A to explain what happens here.)



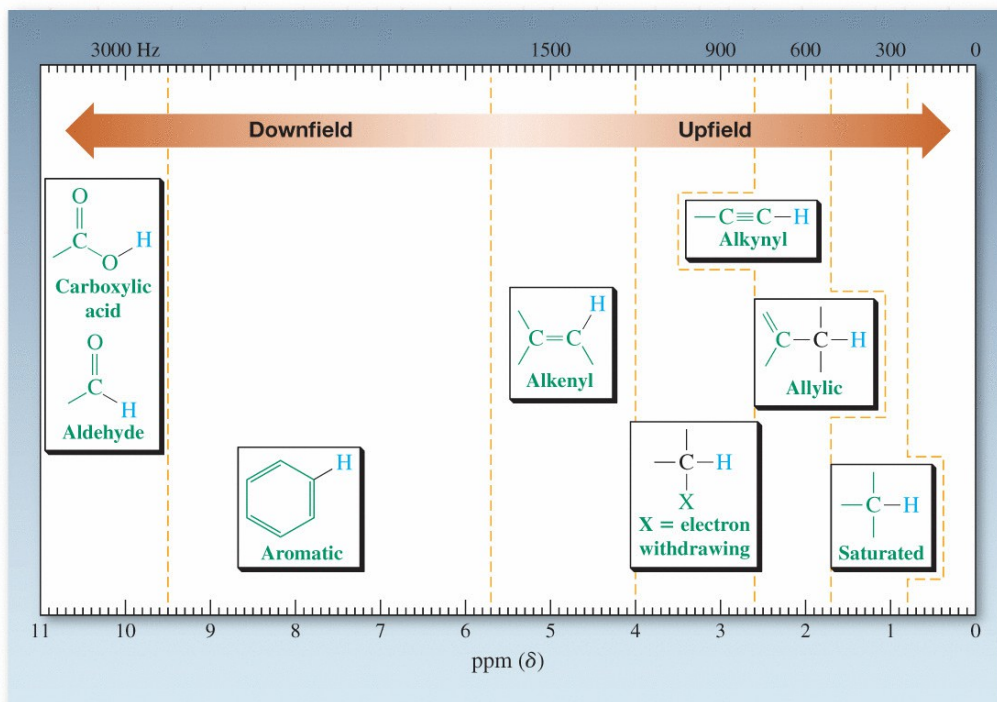
The reverse would happen here: the diene MOs will be stabilized, and the alkene MO's pushed up. The best interaction will be the diene LUMO interacting with the dienophile HOMO.

EWG = Electron-Withdrawing Group  
EDG = Electron-Donating Group

**Table 10-2 Typical Hydrogen Chemical Shifts in Organic Molecules**

Type of hydrogen <sup>a</sup>	Chemical shift $\delta$ in ppm
Primary alkyl, $\text{RCH}_3$	0.8–1.0
Secondary alkyl, $\text{RCH}_2\text{R}'$	1.2–1.4
Tertiary alkyl, $\text{R}_3\text{CH}$	1.4–1.7
Allylic (next to a double bond), $\text{R}_2\text{C}=\text{C}(\text{CH}_3)\text{R}'$	1.6–1.9
Benzylic (next to a benzene ring), $\text{ArCH}_2\text{R}$	2.2–2.5
Ketone, $\text{RC}(=\text{O})\text{CH}_3$	2.1–2.6
Alkyne, $\text{RC}\equiv\text{CH}$	1.7–3.1
Chloroalkane, $\text{RCH}_2\text{Cl}$	3.6–3.8
Bromoalkane, $\text{RCH}_2\text{Br}$	3.4–3.6
Iodoalkane, $\text{RCH}_2\text{I}$	3.1–3.3
Ether, $\text{RCH}_2\text{OR}'$	3.3–3.9
Alcohol, $\text{RCH}_2\text{OH}$	3.3–4.0
Terminal alkene, $\text{R}_2\text{C}=\text{CH}_2$	4.6–5.0
Internal alkene, $\text{R}_2\text{C}=\text{CH}\text{R}'$	5.2–5.7
Aromatic, $\text{ArH}$	6.0–9.5
Aldehyde, $\text{RCH}(\text{O})\text{H}$	9.5–9.9
Alcoholic hydroxy, $\text{ROH}$	0.5–5.0 (variable)
Thiol, $\text{RSH}$	0.5–5.0 (variable)
Amine, $\text{RNH}_2$	0.5–5.0 (variable)

<sup>a</sup>R, R', alkyl groups; Ar, aromatic group (not argon).



**Table 10-6** Typical  $^{13}\text{C}$  NMR Chemical Shifts

Type of carbon	Chemical shift $\delta$ (ppm)
----------------	-------------------------------

Primary alkyl, $\text{RCH}_3$	5–20
Secondary alkyl, $\text{RCH}_2\text{R}'$	20–30
Tertiary alkyl, $\text{R}_3\text{CH}$	30–50
Quaternary alkyl, $\text{R}_4\text{C}$	30–45
Allylic, $\text{R}_2\text{C}=\underset{\text{R}''}{\text{C}}\text{CH}_2\text{R}'$	20–40
Chloroalkane, $\text{RCH}_2\text{Cl}$	25–50
Bromoalkane, $\text{RCH}_2\text{Br}$	20–40
Ether or alcohol, $\text{RCH}_2\text{OR}'$ or $\text{RCH}_2\text{OH}$	50–90
Carboxylic acids, $\text{RCOOH}$	170–180
Aldehyde or ketone, $\text{RCH}=\overset{\text{O}}{\parallel}$ or $\text{RCR}'=\overset{\text{O}}{\parallel}$	190–210
Alkene, aromatic, $\text{R}_2\text{C}=\text{CR}_2$	100–160
Alkyne, $\text{RC}\equiv\text{CR}$	65–95

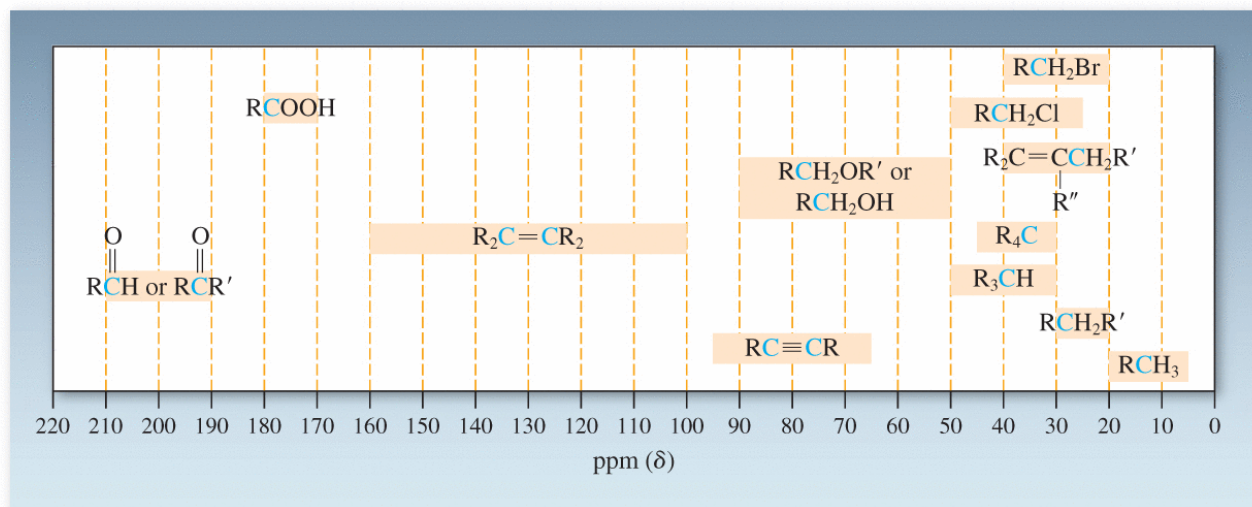
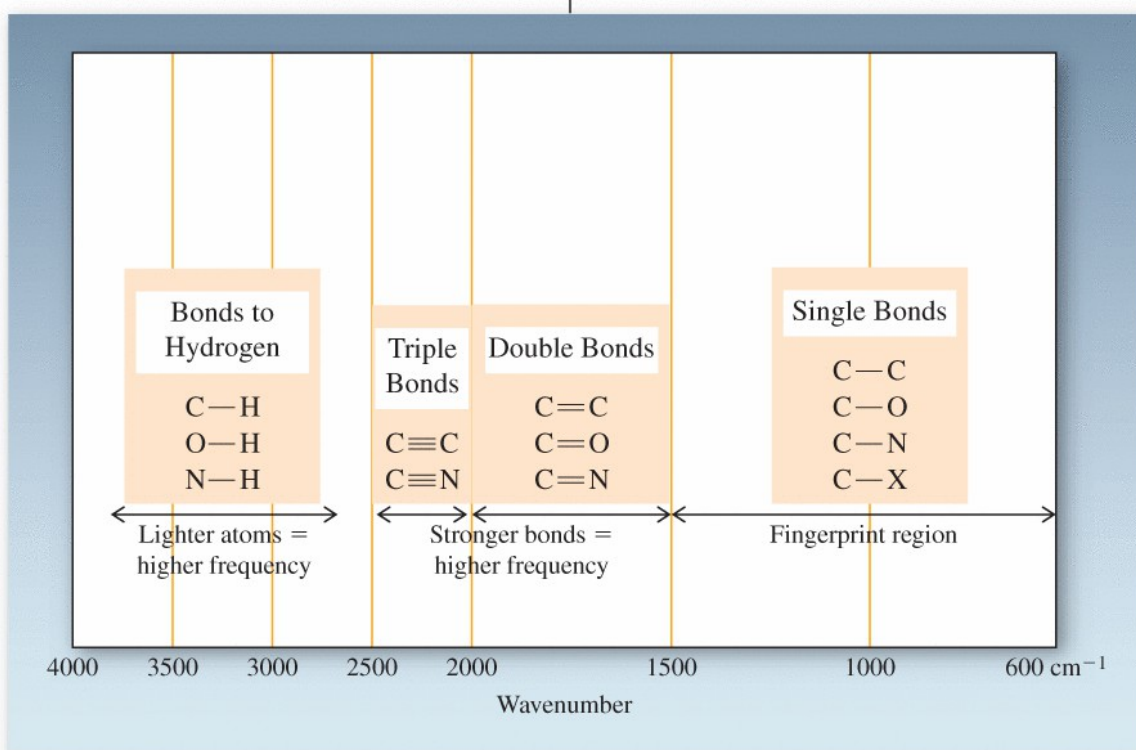


Table 11-4

### Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or Functional Group	$\tilde{\nu}$ ( $\text{cm}^{-1}$ )	Bond or Functional Group	$\tilde{\nu}$ ( $\text{cm}^{-1}$ )
RO—H (alcohols)	3200–3650	RC $\equiv$ N (nitriles)	2220–2260
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCO—H} \end{array}$ (carboxylic acids)	2500–3300	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{RCH, RCR}' \end{array}$ (aldehydes, ketones)	1690–1750
R <sub>2</sub> N—H (amines)	3250–3500	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOR}' \end{array}$ (esters)	1735–1750
RC $\equiv$ C—H (alkynes)	3260–3330	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOH} \end{array}$ (carboxylic acids)	1710–1760
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$ (alkenes)	3050–3150	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$ (alkenes)	1620–1680
$\begin{array}{c}   \\ \text{—C—H} \\   \end{array}$ (alkanes)	2840–3000	$\begin{array}{c}   \\ \text{RC—OR}' \\   \end{array}$ (alcohols, ethers)	1000–1260
RC $\equiv$ CH (alkynes)	2100–2260		

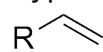

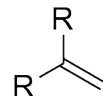

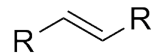
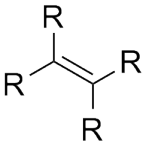


← Increasing wavenumber (energy)

Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH <sub>3</sub> -H	105
CH <sub>3</sub> CH <sub>2</sub> -H	101
(CH <sub>3</sub> ) <sub>2</sub> CH-H	98.5
(CH <sub>3</sub> ) <sub>3</sub> C-H	96.5
CH <sub>3</sub> -F	110
CH <sub>3</sub> -Cl	85
CH <sub>3</sub> -Br	70
CH <sub>3</sub> -I	57
CH <sub>3</sub> CH <sub>2</sub> -F	111
CH <sub>3</sub> CH <sub>2</sub> -Cl	84
CH <sub>3</sub> CH <sub>2</sub> -Br	70
CH <sub>3</sub> CH <sub>2</sub> -I	56
(CH <sub>3</sub> ) <sub>2</sub> CH-F	111
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl	84
(CH <sub>3</sub> ) <sub>2</sub> CH-Br	71
(CH <sub>3</sub> ) <sub>2</sub> CH-I	56
(CH <sub>3</sub> ) <sub>3</sub> C-F	110
(CH <sub>3</sub> ) <sub>3</sub> C-Cl	85
(CH <sub>3</sub> ) <sub>3</sub> C-Br	71
(CH <sub>3</sub> ) <sub>3</sub> C-I	55

Typical Heats of Hydrogenation

	-30 kcal/mol		-28.2 kcal/mol
	-27.9 kcal/mol		-26.5 kcal/mol
	-27.4 kcal/mol		-26.3 kcal/mol